

Synthesis and Structure of Conducting Polymers

Description: The Conducting Polymer Group applies an interdisciplinary approach to the synthesis and characterization of ion conducting polymers. The focus of the program is to design and synthesize new functional groups and new ionic conducting polymers based on the studies of ion-ion and ion-polymer interactions in non-aqueous electrolytes. X-ray absorption and Raman spectroscopy studies indicate ion pairing and cluster formation in non-aqueous electrolytes. All conventional non-aqueous electrolyte solvents, including poly(ethylene oxide), are Lewis bases that interact strongly with cations. The new approach, at BNL, is to modify the solvent chemistry to enhance anion-solvent interactions, by adding new Lewis acid compounds, synthesized at BNL, to the solvent. The compounds form complexes with the anions, dissociate the ion pairs, and free the cations. Therefore, the number of charge carriers, the conductivity and the Li^+ ion transference number are all increased significantly. Characterization includes electrochemical and conductivity studies and the use of a wide array of spectroscopic techniques, such as x-ray absorption spectroscopy (XAS), to elucidate ion-ion and ion-solvent interactions. A successful CRADA with Gould, Inc. of Cleveland, OH on electrolyte additives and characterization of battery cathode materials by high-resolution *in situ* x-ray diffraction (XRD) and XAS was recently completed.

Program Highlights:

We have synthesized a new family of anion-complexing additives based on boron compounds with various fluorinated aryl or alkyl groups. The compounds can be boranes, borates or boronates. These have electron deficient boron sites that interact strongly with anions and break up ion pairs. The result is improvement in electrolyte conductivity and Li^+ ion transference. Furthermore, these additives promote the dissolution of several lithium salts that are normally insoluble in non-aqueous solvents. For instance, the additives increase the solubility of LiF in non-aqueous solvents from $<10^{-5}$ M to >1.0 M. This opens up a completely new approach to the development of liquid and polymer electrolytes using inexpensive and more environmental friendly salts such as LiF . Low cost LiMn_2O_4 cathodes are not stable in conventional LiPF_6 -based electrolytes at elevated temperatures, since LiPF_6 can decompose to yield PF_5 which attacks the organic solvents to yield acidic species. The acidic species cause disproportionation of Mn(III) to yield soluble Mn(II) . Our new LiF based electrolytes are thermally stable and permit the use of LiMn_2O_4 cathodes at elevated temperatures.

The CRADA with Gould Electronics, Inc. resulted in the development of *in situ* high-resolution XRD techniques to study cathode materials for lithium batteries. This has resulted in the discovery of phase formations, during cycling of LiMn_2O_4 , LiCoO_2 and LiNiO_2 , that were not hitherto observed using conventional x-ray sources.

Impact:

- The new anion complexing agents have attracted the attention of many organizations including IBM, Merck, Honeywell, Duracell, Panasonic, Mitsubishi Chemical and Daikin Corp.
- Because of our work on XAS of conducting polymers we were asked to collaborate with PNNL on a DOE-EM program on the use of conductive polymers in nuclear waste cleanup. This program has recently been renewed.
- *In situ* high-resolution XRD has led to important insights regarding the high temperature stability of LiMn_2O_4 .

Interactions:

University collaborations include SUNY Stony Brook, Northeastern University and Polytechnic University. Industrial collaborations include Gould Electronics, Inc., FMC Corp., 3M Corp., and Gillette (Duracell) Government Laboratory interactions include ARL, NRL and PNNL

Personnel:

J. McBreen (project leader), X. Q. Yang (materials characterization), H. S. Lee (materials synthesis), X. Sun (synthesis and characterization), M. Balasubramanian (new characterization methods at NSLS)

Recognition:

Ten invited presentations in the past year.

Two U.S. patents awarded in past year.

J. McBreen was elected Fellow of The Electrochemical Society, September 2001

J. J. Reilly is the recipient of the 2002 Design and Engineering Award from Popular Mechanics magazine.

Budget: \$413 K

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List of Scientific Staff and Areas of Expertise:

James McBreen	Principal Areas of Research and Expertise: Electrochemistry, electrocatalysis, hydrogen in metals, batteries and the application of synchrotron methods to electrolytes and electrode materials.
X. Q. Yang	Principal Areas of Research and Expertise: Optical and electronic properties of conducting polymers, synchrotron-based x-ray absorption and diffraction for studying conductive polymers, electrolyte, and electrode materials.
H. S. Lee	Principal Areas of Research and Expertise: Organic synthesis, synthesize optically active and electroresponsive polymers.
X. Sun	Principal Areas of Research and Expertise: Synthesis and characterization of optically active and electroresponsive polymers. Application of synchrotron methods to electrolytes and electrode materials.
M. Balasubramanian	Principal Areas of Research and Expertise: Structural vibrational and electronic properties of novel and advanced materials. Application of <i>in situ</i> synchrotron methods to and electrode materials and polymers.

Other Sources of Funding

DOE, EE	Diagnostics of Power Fade Mechanisms in Lithium Ion Batteries	\$355K
	Battery Materials: Structure and Characterization	\$150K
	Characterization of Fuel Cell Electrocatalysts	
DOE, EW	Conductive Polymers for Anion Separation in Nuclear Waste	\$50K

Facilities

Synthesis and characterization facilities for organic compounds and polymers, TGA. DSC thermal analysis instruments, four and eight channel battery cyclers.

PRT member of X11A, X23B and X18A at NSLS, general users of U7A, X7A, and X19A.

Future Directions

- Design, synthesis and characterization of polymer and gelled electrolytes with Lewis acid centers
- X-ray Raman studies of polymer electrolytes
- Cation conducting polymers with conductivities $>10^{-4}$ S/cm at 25 °C
- Collaborating with Prof. Ben Chu and Prof. Ben Hsiao at SUNY Stony Brook, develop functional nanomaterials for batteries and fuel cells.
- Collaborating with Prof. Clare Grey at SUNY Stony Brook, develop nanomaterials for lithium battery cathodes and anodes.

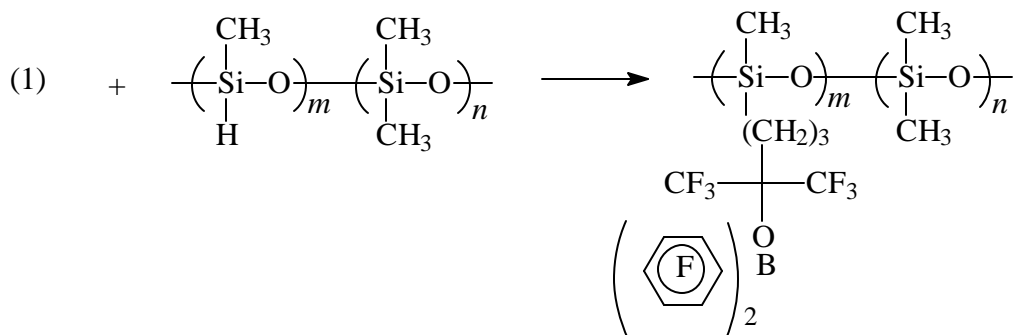
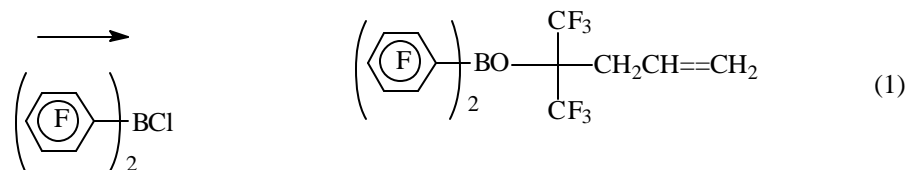
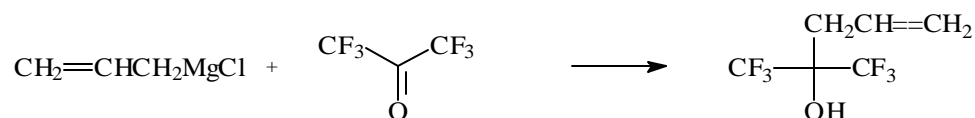
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Example of future plans

We will focus our efforts on design, synthesis, and characterization of polymer and gelled polymer electrolytes with Lewis acid centers.

One simple approach is blending the boron based compounds with lithium salts, polymers (PEO or other polymers), and non-aqueous solvents.

A more sophisticated approach is the grafting of boron based functional groups to the polymer backbone, followed by cross-linking the polymer to increase the mechanical strength. This approach had been successfully used with our aza compounds, and we will apply it to the boron compounds next. Several polymers, such as polysiloxane, and polystyrene will be used. Here is one example of a scheme for grafting the boron based functional groups on polysiloxane.



LiF or CF_3COOLi



Cross linker

gel polymer

List of External Collaborators and Institutions

Polytechnic University - Y. Okamoto
SUNY Stony Brook - C. Grey, B. Hsaio, B. Chu
Northeastern University - S. Mukerjee
Rutgers University – J. J. Xu
Saga University – M. Yoshio
Waseda University – H. Nishide
University of Sao Paulo, Sao Carlos – E. A. Ticianelli
Naval Research Laboratory - L. S. Choi
NIST D. Fischer
Pacific Northwest National Laboratory - T. L. Hubler
Osaka National Research Institute – T. Sakai, Y. Xia
Power Conversion, Inc. - J. Drass
Gould Electronics, Inc. - M. L. Daroux, X. K. Xing
3M Corp - R. Atanasoski
FMC Corp. - Y. Gao
The Gillette Company – W. Bowden
Telecordia – G. Amatucci

List of BNL Collaborators

Soft x-ray XAS studies of electrodes and materials, A. Moodenbaugh, Materials Science Department
In situ XRD studies of electrode materials, T. Vogt, Physics Department
K- β x-ray emission and x-ray Raman studies of oxides and polymers, C. C. Kao, NSLS

Accomplishments

Much of the early work on polymer electrolytes was of a macroscopic nature wherein correlations were made between the phase diagrams of the electrolytes and their ionic conductivity. More recently the focus is on interactions at the microscopic level on phenomena such as ion-polymer interactions, ion pairing, polymer chain cross-linking and salt precipitation. At the time of the last review considerable progress had been made at BNL in understanding these factors, using Raman and x-ray absorption spectroscopy (XAS). Since then most of the effort has been devoted to the synthesis and characterization of new functional groups and new electrolytes that minimize ion pairing. Ion pairing in conventional non-aqueous liquid and polymer solvents occurs because these are Lewis bases. Lewis base sites such as the lone pair electrons on the oxygen in poly(ethylene oxide) can accommodate cations. However, they cannot accommodate anions. This causes the ion pairing which reduces ionic conductivity and Li^+ ion transference.

The synthetic approach is the use of Lewis acid anion complexing agents to promote ion dissociation and Li^+ ion transference number. Anion receptors are a very active field of research with most of the work aimed at molecular recognition to mimic how ion-binding proteins control ion transport in biological membranes. Present anion receptors are based either on positively charged sites, hydrogen bonding, or Lewis acid metal centers. None of these are suitable for use in non-aqueous electrolytes. At BNL we have synthesized two new families of stable anion complexing agents. One of these is based on aza compounds and they greatly increase the conductivity of non-aqueous electrolytes, such as lithium salt solutions in tetrahydrofuran (THF). They are either cyclic, linear or branched aza compounds in which the H on the N is replaced by an electron-withdrawing group such as CF_3SO_2^- . The electron-withdrawing group imparts a small positive charge to the N atoms, enable the compound to complex anions. They function with anions in much the same way as crown ethers act with cations. This has been confirmed in extensive XAS studies in LiBr, LiCl solutions in non-aqueous solvents at the respective Br and Cl K edges and in LiI at the I L_1 edge. At BNL we have synthesized several polymer electrolytes, based on the complexing of anions, by grafting the aza anion acceptors onto siloxane polymer backbones. The polymers can dissolve lithium salts such as LiCl to yield a totally new type of polymer electrolytes that do not contain ethylene oxide groups. XAS confirmed complexing of the Cl^- in the polymer.

The main shortcomings of the aza anion receptors are their high molecular weight, low solubility in non-aqueous solvents and instability at elevated temperatures. More recently, based on the extensive knowledge gained from the aza compounds, we have designed and synthesized another family of boron based anion complexing agents. These compounds are based on electron deficient boron sites on borane, borate or boronate compounds with various fluorinated aryl or alkyl groups. Some of the boron-based anion receptors can promote the dissolution of normally insoluble salts, such as LiF, in several non-aqueous solvents. The additives increase the solubility of LiF in non-aqueous solvents from $<10^{-5}$ M to >1.0 M and the conductivity from 10^{-6} S/cm to 3×10^{-3} S/cm. This has never been accomplished before. The anion complexation power, the effects on ion pair dissociation, the thermal and electrochemical stability, and their relationships with the structure of boron compounds have been studied with various types of spectroscopic experiments, such as XAS, cyclic voltammetry, and TGA. The near edge x-ray absorption spectra of some boron based anion receptors are plotted in Fig. 1 and Fig. 2. together with their conductivities. Recently, a new family of boronate compounds has been designed and synthesized with their high solubility and compatibility with polymers. Examples of the chemical structures of these boronate compounds are plotted in Fig. 3. Low cost LiMn_2O_4 cathodes are not stable in the LiPF_6 based electrolytes, now used in lithium ion batteries. The problem is exacerbated at elevated temperatures, since LiPF_6 can decompose to yield PF_5 which attacks the organic solvents to yield acidic species. The acidic species cause disproportionation of Mn(III) to yield soluble Mn(II). Our LiF based electrolytes are thermally stable and permit the use of LiMn_2O_4 cathodes at elevated temperatures. Several LiF based electrolytes of this type have been successfully evaluated in rechargeable Li/ LiMn_2O_4 batteries. Most of the boron based anion receptors have high solubility in conventional non-aqueous solvents. Several of the compounds have exceptional chemical, electrochemical and thermal stability. Using these materials will facilitate the synthesis of new electrolytes and utilize inexpensive and more environmental friendly lithium salts that are normally not soluble in non-aqueous solvents. With the recent commercialization of gel type polymer electrolyte based lithium ion batteries in 1999, research on additives and functional groups which can be blended or grafted on polymers has intensified. Our new approach of using boron based anion receptors as additives or functional groups in gel type electrolytes has attracted great attention from both the academic and industrial communities. Panasonic invited us to present our results at their Battery research and Development Center near Osaka. Scientists from Mitsubishi Chemical and Daikin Corp. visited BNL to discuss the possible collaboration. Duracell (Gillette) also expressed their interest in these materials. We are now designing and synthesizing versions of these anion complexing agents that are suitable for gelled electrolytes. The approach is to make them soluble in PEO or can be grafted onto polymer backbones.

In the CRADA with Gould Electronics, Inc., a key player in developing lithium polymer batteries, *in situ* x-ray diffraction (XRD) techniques have been developed for the study of oxide cathodes for lithium-ion batteries. Most of the work has been on LiMn_2O_4 spinel, LiNiO_2 and LiCoO_2 materials. With the high intensity synchrotron x-ray beam it is possible to do the XRD in the transmission mode using a simple spectroelectrochemical cell. In the case of all of these materials the results reveal phase transitions that cannot be seen in *in situ* experiments with conventional x-ray sources. One important discovery is the identification of a new cubic phase for LiMn_2O_4 cathode during charge. This new phase transition has been recognized as responsible for capacity fading of this material by several recent studies including work at Sony Corp. The *in situ* XRD spectra of this material during charge are plotted in Fig. 4.

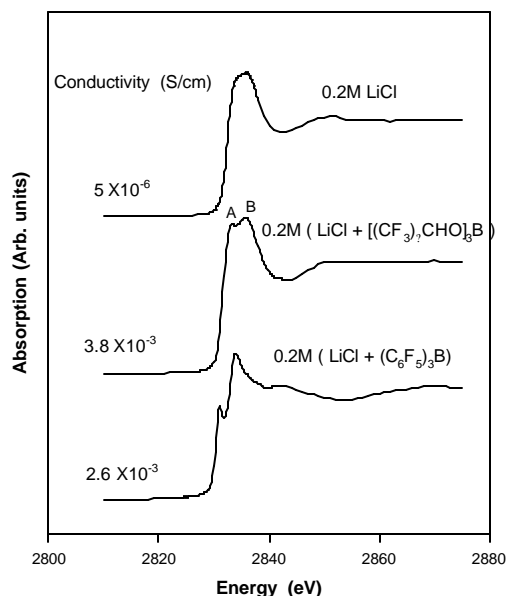


Fig. 1 Near edge Cl K edge x-ray absorption spectra for LiCl in DME solution and LiCl with boron based anion receptors in DME solution

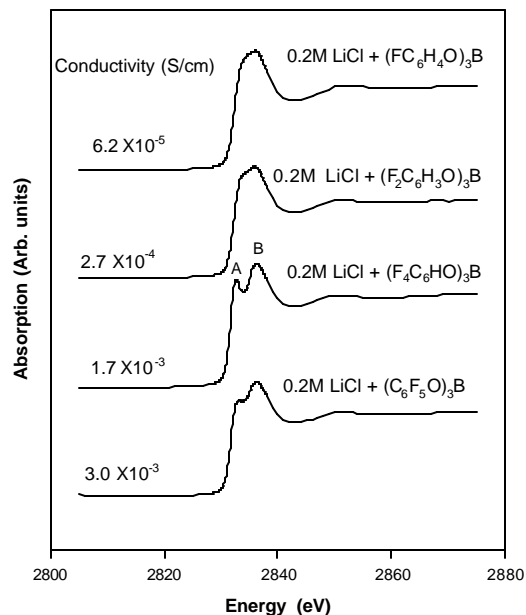


Fig. 2. Effects of degree of fluorination of borate on conductivity and the near edge (Cl K edge) white line splitting in DME solution

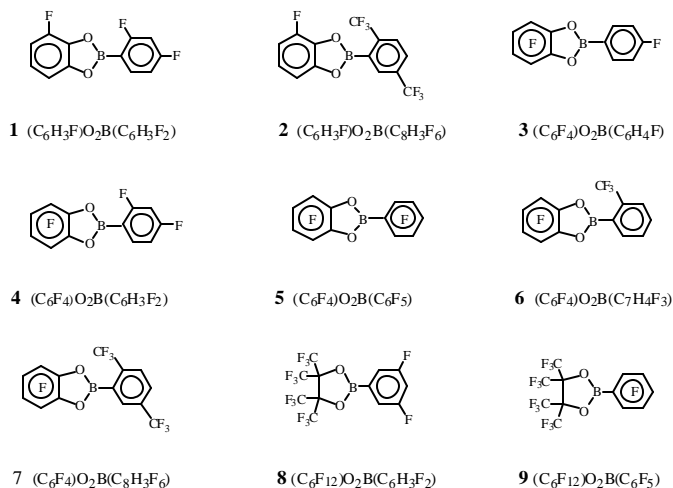


Fig. 3. Chemical structures of recently designed and synthesized boronate based anion receptors

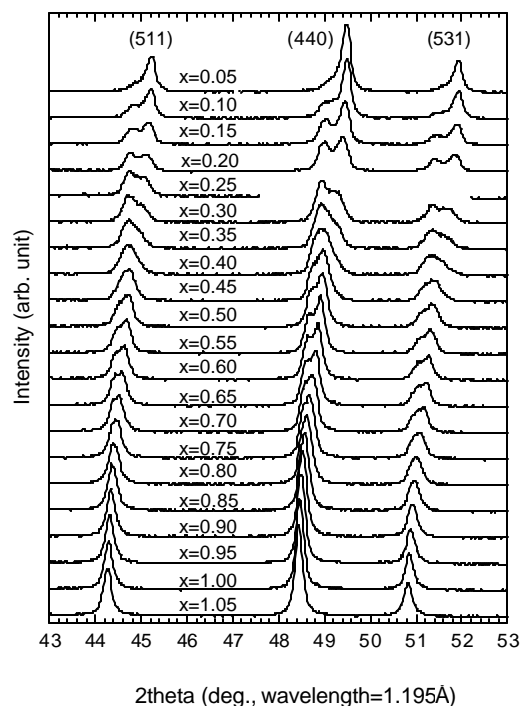


Fig. 4. In situ XRD spectra for $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode material during the first charge, showing the presence of three cubic phases.

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3. H. Nishide, H. Mizuma, E. Tsuchida and J. McBreen, Reversible stretching of a polymer-supported cobalt-chelate film in response to oxygen, *Bull. Chem. Soc. Jpn.*, **72**, 1123 (1999).
4. X. Sun, H. S. Lee, X. Q. Yang and J. McBreen, Comparative studies of electrochemical and thermal stability of two types of composite lithium battery electrolytes using boron-based anion receptors, *J. Electrochem. Soc.*, **146**, 3655 (1999).
5. W. B. Heuer, H. S. Lee and O.-K. Kim, Influence of hemicyanine dye structures on spectral properties of their supramolecular complexes with amylose, *Chem. Commun.*, 2649 (1998).
6. X. Q. Yang, X. Sun and J. McBreen, New findings on the phase transitions in $\text{Li}_{1-x}\text{NiO}_2$: *In situ* synchrotron x-ray diffraction studies, *Electrochem. Commun.*, **1**, 227 (1999).
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8. H. S. Lee, X. Sun, X. Q. Yang, J. McBreen and L. S. Choi, Synthesis of cyclic aza-ether compounds and studies of their use as anion receptors in non-aqueous lithium halide salts solutions, *J. Electrochem. Soc.*, **147**, 66 (2000).
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13. X. Sun, H. S. Lee, X. Q. Yang and J. McBreen, Improved elevated temperature cycling of LiMn_2O_4 spinel through the use of a composite LiF based electrolyte, *Electrochem. Solid-State Lett.*, **4**, A184 (2001).
14. M. T. Giacomini, E. A. Ticianelli, J. McBreen and M. Balasubramanian, Oxygen reduction on supported platinum/polythiophene electrocatalysts, *J. Electrochem. Soc.*, **148**, A323 (2001).
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18. X. Sun, X. Q. Yang, H. S. Lee and J. McBreen, Electrochemical and thermal stability studies of composite electrolytes containing boron-based anion receptors for lithium batteries, Proc. Symp. on Lithium Batteries, 196th Meeting of the Electrochemical Society, Honolulu, HI, Oct 17-22, 1999.
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- materials. Proc. Symp. on Lithium Batteries, 196th Meeting of the Electrochemical Society, Honolulu, HI, Oct 17-22, 1999.
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 27. J. McBreen, H. S. Lee, and X. Q. Yang, “Synthesis of a New Family of Fluorinated Boronate compounds as Anion Receptors and studies of their use as Additives in Lithium Battery Electrolytes”, p59, Proceedings of China International Battery Fair 2001, Beijing, China June 8-11, 2001.

Patents:

H. S. Lee, X. Q. Yang, J. McBreen and C. Xiang, Boron compounds as anion binding agents for non-aqueous battery electrolytes, U.S. Pat. 6022643, Feb. 8, 2000.

H. S. Lee, X. Q. Yang and J. McBreen, Anion receptor compounds for non-aqueous electrolytes, U. S. Pat. 6120941, Sept. 19, 2000.